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(54) Title: PROCESS FOR THE PRODUCTION OF ALCOHOLS (57) Abstract A process for the manufacture of alcohols by liquid phase catalytic hydrogenation of mono- or dicarboxylic acids or their esters in which the hydrogenation is carried out in the presence of a liquid, inert hydrogen carrier. Preferably, the reaction conditions are such that the hydrogen carrier is in a supercritical state.		

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PROCESS FOR THE PRODUCTION OF ALCOHOLS

This invention relates to a process for the manufacture of alcohols by liquid phase catalytic hydrogenation of
5 carboxylic acids or their esters. Preferably the carboxylic acids are monocarboxylic acids having from 6 to 24 carbon atoms, and their esters are preferably derived from monohydric alcohols having from 1 to 24 carbon atoms, thus also including waxes.

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The most common technology for the commercial production of fatty alcohols is a liquid phase hydrogenation process in which fatty acids or their alkyl esters are converted into fatty alcohols at 200-300 bar hydrogen pressure at
15 temperatures between 200-300°C in the presence of usually a copper/chromite catalyst. Two moles of hydrogen are necessary for the conversion of one mole of fatty acid into fatty alcohol. It is well known that hydrogen is poorly soluble in organic mediums like fatty acids or their
20 esters, particularly at high temperature. Therefore, a high hydrogen pressure is necessary to dissolve sufficient hydrogen to drive the reaction to completion and to achieve a high selectivity. At hydrogen pressures below 200 bar the hydrogen solubility decreases as a result of which the
25 selectivity decreases, leading to the formation of fatty acid-fatty alcohol esters, which must be recirculated, and hydrocarbons which are undesired contaminants. The capital investments for a fatty alcohol plant operating at these process conditions are high, particularly if the excess of
30 hydrogen gas used has to be recirculated at the high pressures involved.

It has therefore been tried to develop a low pressure hydrogenation process, i.e. a pressure below 100 bar, for
35 the manufacture of fatty alcohols from fatty acids, which would lower the investment costs.

Thus, in British Patent Specification GB-A-433,549 (I.C.I. Ltd) it has been proposed to manufacture alcohols by hydrogenating the corresponding fatty acids or esters thereof in the presence of a catalyst at a pressure below 5 50 atmospheres (but which may be as low as 5 atmospheres). This low pressure is possible by vigorously stirring the substance to be hydrogenated and the catalyst, whilst rapidly passing through hydrogen, whereby the alcohols formed are carried out of the reaction vessel in the stream 10 of hydrogen as they are formed. It will be clear that in such a way large amounts of hydrogen are involved and a rather complicated recirculation system will be necessary.

15 In another proposal fatty acids or their lower alkyl esters are hydrogenated at a hydrogen pressure of 25 to 100 bar and a temperature of 200°C-300°C (British Patent Specification GB-A-2,143,524 (Oleofina S.A.)). This relatively low pressure is possible only if a specific, 20 two-component catalyst is used, viz. a catalyst consisting of (i) a Cu-Cr mixture, and (ii) Cu deposited on a support. In an example methyl laurate is hydrogenated at 60 bar and 218°C to lauryl alcohol in a yield of 97,5%. Although the hydrogen flow has not been mentioned, it still must be 25 appreciable.

All these known processes are catalytic hydrogenations in the liquid phase. If the hydrogenation is carried out in the vapour phase, however, a lower hydrogen pressure may be 30 used.

Thus, in German Patent Specification DE-A-1,275,042 (Kyowa Hakko Kogyo Ltd) it has been proposed to manufacture saturated alcohols and saturated carbonyl compounds by catalytic hydrogenation of alpha, beta-unsaturated carbonyl 35 compounds in the vapour phase at a pressure of 1-3 atmospheres, in the presence of a lower saturated alkane (methane, ethane or propane). On the one hand this

alkane prevents that the catalyst mass will be locally overheated, but on the other hand a difference in the hydrogenation velocities of the olefinic double bond and of the carbonyl group is effected. If the amount of saturated alcohol formed should be increased, then the amount of alkane should be as low as possible.

Recently, Davy McKee published in Oils and Fats International, Issue III, 1990, also a new process operating at low hydrogen pressure. The technology is based on the conversion of fatty acid methyl esters in the vapour phase into fatty alcohols at 40 bar and 200-250°C in the presence of a non-disclosed catalyst. Vaporization of the methyl esters is achieved by a hot hydrogen recycle stream. The combination of a vapour phase reaction and mild reaction conditions (low hydrogen pressure, lower temperatures) is claimed to minimize by-product formation.

The applicability of the Davy McKee process (which has also been described in British Patent Specification GB-A-2,116,552) is limited by the volatility of the starting material. The process becomes unattractive for the manufacture of long chain alcohols. The volatility of long chain fatty acid methyl esters such as C₁₆ and C₁₈ fatty acid methyl esters is too low, necessitating an excessively high hydrogen gas recycle flow for their vaporization. A large hydrogen gas-recycle flow is also still necessary for the complete vaporization of short chain methyl esters. Consequently, the energy input for gas recirculation is high.

There is therefore still a need for a liquid phase hydrogenation process for the conversion of especially fatty acids or their alkyl esters into fatty alcohols, operating at low hydrogen pressure with a very limited hydrogen recycle, resulting in high conversion and selectivity.

It has now been found that if the catalytic hydrogenation in the liquid phase is carried out in the presence of a liquid, inert hydrogen carrier, i.e. an inert solvent in which a relatively large amount of hydrogen can be dissolved at the conditions of the reaction, the reaction can be effected at a low hydrogen pressure without volatility limitations. The use of this liquid, inert hydrogen carrier at the same time decreases the concentration of the substance to be hydrogenated in the reaction medium and consequently the molar ratio of hydrogen to substance to be hydrogenated is favoured, allowing the reaction to proceed at relatively low hydrogen pressure, with a high degree of conversion and a high selectivity, independent of the chain length of the fatty acid.

Therefore, the present invention relates to a process for the manufacture of alcohols by liquid phase catalytic hydrogenation of carboxylic acids or their esters, characterized in that the hydrogenation is carried out in the presence of a liquid, inert hydrogen carrier.

By "liquid" is understood throughout this specification and the attached claims in liquid form either at room temperature and atmospheric pressure (15°C; 98.1 kPa) or at the conditions of the reaction. In this latter case, the hydrogenation reaction is carried out under supercritical conditions for the inert hydrogen carrier, and such a reaction is preferred.

In principle, any liquid inert hydrogen carrier can be used in the process of the present invention. The factors determining the choice of the liquid inert hydrogen carrier are the solubilities of hydrogen, of the material to be hydrogenated, and of the alcohol which is formed in the hydrogenation reaction in the hydrogen carrier and the ease of separation from the alcohol after completion of the

reaction. The solubility of hydrogen in the liquid inert hydrogen carrier is an important criterium. It is determined by the polarity and the molecular weight of the liquid inert hydrogen carrier. To facilitate separation by distillation, the liquid inert hydrogen carrier should have either a distinctly lower or a distinctly higher volatility than the alcohol formed in the hydrogenation reaction.

Suitable liquid inert hydrogen carriers are preferably selected from hydrocarbons such as alkanes, cycloalkanes, aromatic hydrocarbons and the like. In particular branched chain alifatic hydrocarbons are preferred in view of the high solubility of hydrogen in such substances. Examples are octane, isooctane and high boiling mineral oils. Also mixtures of hydrocarbons can be used. Another class of materials are the wax esters, fatty acid esters of fatty alcohols.

In a particular embodiment of the present invention the hydrogenation is effected under supercritical conditions by using a low boiling alkane, such as pentane. The advantage of working under critical conditions with low boiling alkanes is the high solubility of hydrogen in the lower alkanes, particularly the branched chain alkanes having up to 10 carbon atoms.

The use of solvents in liquid phase catalytic hydrogenation processes is known, for example from European Patent Specification EP-A-0,319,208 (Davy McKee Ltd) but in this case such solvents are used to limit the temperature rise due to the exothermic character of the hydrogenation reaction, particularly when the hydrogenation zone is operated under adiabatic conditions.

The solvent in this publication can be supplied either in the form of an inert gas admixed with the hydrogen in an amount up to 50 mole%, or as a diluent added to the feed stock to be hydrogenated. Usually, the hydrogenation

product itself is used for that purpose and therefore part of the hydrogenation product is recycled and admixed with the feedstock to be hydrogenated.

- 5 This same principle has also been disclosed in catalytic liquid phase hydrogenations, using an excess of hydrogen, so as to entrain and remove the liquid or gaseous reaction products formed, as has for example been disclosed in United States Patent Specification US-A-3,565,921 (Melle-
10 Bezons S.A.).

- Raw materials that can be used in the process of the present invention are monocarboxylic acids having 6-24 carbon atoms and dicarboxylic acids having 6-36 carbon
15 atoms, such as 2-ethylhexanoic acid, stearic acid, adipic acid and dimerized fatty acid, or their alkyl esters with alkanols having 1-24 carbon atoms, such as methanol or octanol. Esters from the said fatty acids with polyhydric
20 alcohols having 2-6 carbon atoms, like glycerol, diethyleneglycol and trimethylolpropane can also be used. For sake of convenience methyl esters are preferably used. The carboxylic acid methyl esters used for the conversion into fatty alcohol according to the invention can be
25 manufactured by interesterification of the corresponding triglyceride with methanol or by esterification of free fatty acids with methanol, applying techniques known in the art.

- The fatty acid methyl ester should be as free as possible
30 from residues of catalyst used in the esterification or interesterification process, which residues may poison the hydrogenation catalyst. It is therefore particular advantageous to carry out the esterification of fatty acid with methanol without a catalyst as disclosed in European
35 Patent Application EP 89203343.3 (Unilever).

The concentration of the material to be hydrogenated in the liquid inert hydrogen carrier is related to the concentration of hydrogen in the hydrogen carrier. The mole ratio hydrogen/material to be hydrogenated is preferably greater than 5, more preferably greater than 20. Ratios greater than 50 can also be used, but may be less preferable in view of the higher hydrogen pressure or the too low feed concentration that may be necessary to achieve such a ratio.

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The process of the present invention allows the use of hydrogen pressures between 20 and 100 bar without excessive recycling of hydrogen. Normally at hydrogen pressures of 30-50 bar already enough hydrogen is dissolved in the liquid inert carrier at reaction temperatures of 185-225°C to achieve an almost complete conversion (over 96%) of the material to be hydrogenated with an extremely high selectivity (over 99%).

20 In the process according to the present invention the carboxylic acids or their esters are admixed with the liquid inert hydrogen carrier and the mixture is saturated with hot hydrogen gas and led over a fixed bed catalyst, preferably of copper-chromium or copper-zinc type at 25 150-275°C and 20-100 bar hydrogen pressure. The crude alcohols formed, leaving the fixed bed reactor, are cooled by heat exchange with the feed and depressurized to separate dissolved hydrogen, which is recirculated. The liquid inert hydrogen carrier is separated from the alcohol 30 and recycled.

The hydrogenation catalysts used in the process according to the present invention can be any of the well-known copper containing catalysts, such as Raney copper, copper chromite, copper-zinc-oxide, copper-zinc-oxide on alumina, 35 and the like. The preparation of such catalysts has inter alia been described in German Patent Specification

DE-A-3,920,288 (Henkel).

The temperature at which the process of the present invention is carried out ranges from 150°C up to 275°C, preferably from 185° to 225°C. Higher temperatures are not necessary and should preferably be avoided to minimize alkane formation.

It has been found that by proper selection of hydrogen carrier, catalyst and reaction conditions, a conversion degree of fatty acid methyl esters to fatty alcohols of over 99% can be obtained, with more than 99% selectivity.

Although the use of a fixed catalyst bed reactor is preferred, the catalytic hydrogenation according to the present invention can also be carried out in a slurry whilst agitating, or in the trickle phase.

The use of such conditions of temperature and pressure and such a type of inert hydrogen carrier that this is in the liquid, supercritical state is a particularly preferred embodiment of the process according to the present invention.

The invention will now be further illustrated on hand of the following examples:

Example 1

A Cu/ZnO/SiO₂ catalyst was prepared by adding:

10 g SiO₂, 7.56 g Cu (NO₃)₂ · 3H₂O, 4.10 g Zn (NO₃)₂ · 4H₂O, 8.47 g urea and 1 kg water together in a stirred vessel. The pH was adjusted to 3 with diluted nitric acid. The mixture was stirred vigourously during 24 hours at a temperature of 90°C. Afterwards the pH became about 7 and the blue precipitate was filtered off hot, thoroughly washed with water and dried at 110°C for 16 hours.

The obtained precursor was calcined at 477°C for 12 hours in air and reduced at 327°C for 12 hours in hydrogen.

A catalyst was obtained containing 77.5 wt%, SiO₂,
5 13.8% Cu (based on Cu metal) and 8.7 wt% ZnO.

A fixed-bed reactor was loaded with 0.1 g of the catalyst thus prepared. The reactor was fed at a rate of 0.1 ml/min with octane as the hydrogen carrier in which was dissolved
10 0.01 mol.dm⁻³ methyl palmitate and 0.32 mol.dm⁻³ hydrogen. The pressure was 40 bar and the temperature 197°C. The methyl palmitate was completely (99%) converted into cetyl alcohol with a selectivity of 99.5%.

15 Example 2

The experiment of Example 1 was repeated with mineral white oil as the hydrogen carrier. The concentration of hydrogen in the white oil was 0.10 mol.dm⁻³. All other reactor conditions were equal to those described in Example 1. The
20 conversion of methyl palmitate was 92% at a selectivity of 99%.

Example 3

The experiment of Example 1 was repeated at the same
25 conditions, except for a feed rate of 0.3 ml/min and a reaction temperature of 207°C. The conversion was practically complete, and the alkane formation was lower than 1%.

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Example 4

The experiment of Example 1 was repeated at the same reaction conditions, but the hydrogen concentration was 0.23 mol.dm⁻³, the pressure was 32 bar and the feed rate
35 was 0.3 ml/min. The conversion of methyl palmitate was 82%, without alkane formation.

Example 5

0.1 g of the catalyst of Example 1 was loaded into a batch autoclave together with 100 ml of a 0.01 mol.dm^{-3} solution of methyl palmitate in octane. The reactor was pressurized with hydrogen at 44 bar and stirred continuously to keep the catalyst in suspension and to enhance the rate of dissolution of the hydrogen. The temperature in the reactor was kept at 197°C . After 24 hours, the methyl palmitate was completely converted at a selectivity of 99.7% into cetyl alcohol.

CLAIMS

1. A process for the manufacture of alcohols by liquid phase catalytic hydrogenation of carboxylic acids or their esters, characterized in that the hydrogenation is carried out in the presence of a liquid, inert hydrogen carrier.
2. A process according to Claim 1, characterized in that the liquid, inert hydrogen carrier is supercritical under the conditions of the hydrogenation reaction.
3. A process according to Claim 1, characterized in that the liquid, inert hydrogen carrier has a lower volatility than the alcohol formed in the hydrogenation.
4. A process according to Claim 1, characterized in that the liquid, inert hydrogen carrier has a higher volatility than the alcohol formed in the hydrogenation.
5. A process according to Claim 1, characterized in that the liquid, inert hydrogen carrier is selected from the group consisting of straight or branched chain alkanes, cyclo-alkanes, aromatic hydrocarbons, wax esters, and mixtures thereof.
6. A process according to Claim 2, characterized in that the inert hydrogen carrier is a straight or branched chain alkane having up to 10 carbon atoms.
7. A process according to Claim 1, characterized in that the carboxylic acid is a monocarboxylic acid having from 6 to 24 carbon atoms.

8. A process according to Claim 1, characterized in that the carboxylic acid is a dicarboxylic acid having from 6 to 36 carbon atoms.
9. A process according to Claim 1, characterized in that the carboxylic acid ester is derived from a monohydric alcohol having from 1 to 24 carbon atoms.
10. A process according to Claim 1, characterized in that the carboxylic acid ester is derived from a polyhydric alcohol having from 2 to 6 carbon atoms.
11. A process according to Claim 1, characterized in that the hydrogenation is carried out at a temperature of 150°C to 275°C, preferably from 175°C to 225°C.
12. A process according to Claim 1, characterized in that the hydrogenation is carried out at a pressure of 20 to 100 bar, preferably from 30 to 70 bar.
13. A process according to Claim 1, characterized in that the catalyst is a copper containing catalyst.
14. A process according to Claim 1, characterized in that the catalyst is a copper containing catalyst, comprising zinc, chromium and iron in metal and/or oxide form.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/EP 93/02383

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C29/149 C07C31/125

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 143 524 (OLEOFINA S.A.) 13 February 1985 cited in the application see page 3 - page 4; claims ---	1
A	EP,A,0 319 208 (DAVY MCKEE LTD) 7 June 1989 cited in the application see page 8, line 20 - line 52 see page 28; claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Fax (+ 31-70) 340-3016

Authorized officer

Kinzinger, J

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Information on patent family members

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